

[0001] The present invention concerns synergistic biocides active substance combinations, of compositions, containing such active substance combinations, and uses of such compositions as preservative to materials and material mixtures, who will strike from harmful microorganisms can.

[0002] In particular the invention concerns the use of such biozider active substance combinations as bundle preservative, preferentially for aqueous dispersions, in particular polymer dispersions and such a thing, in addition, for the inset in paints, flashes, Ligninsulfonaten, chalk mixing into a paste with, adhesives, photo chemicals, caseinhaltigen products, stärkehaltigen products, bitumen emulsions, Tensidlösungen, fuels, cleaning agents, cosmetic products, water circulations, polymer dispersions and Kühlschmierstoffen against the infestation through for example bacteria, filament eye of funguses, yeast and algae.

[0003] The term ?polymer dispersion? is a collective term for dispersions (Latices) of finely divided natural and/or synthetic polymers (usual particle size 0.05-5 mm) in usually aqueous, more rarely not-aqueous dispersing agents. Thereby dispersions of polymers are enclosed such as nature (rubber latex) and synthetic rubber (Syntheselatex), as also by synthetic resins (synthetic resin dispersions) and plastics (plastic dispersions) like polymers, polycondensates and polyaddition compounds. One differentiates between primary dispersions, with which the polymerisation that takes place basis monomers directly in the liquid phase (suspension polymerisation or emulsion polymerisation, z. B. of vinyl acetate od. Acrylates) and secondary dispersions, with which prefabricated polymers in a second process step are dispersed (z. B. of polyisobutene, silicone resins, PU, polyvinyl ethers).

[0004] Polymer dispersion find use in paints (dispersion, Latex, binder paints), in the building and corrosion protection, in the paper, textile and carpet coating, for Latexschaumformteile, as adhesives and so on.

[0005] Polymer dispersions offer a good fertile soil to ways of the often high content of organic material, which is present in aqueous environment, for certain microorganisms. It is advisable to protect it by a preservative against the infestation and decay.

[0006] Preservatives are antimicrobial materials, those with the production process a product (food or luxury, pharmaceutical, cosmetic or also chemical-technical preparing) in small quantities (usual depending upon product between approx. 0.0005% and 1% active content) to be added. Preservatives are to protect products in particular during the making, the storage and the use against impurities by microorganisms against the mikrobiell caused unfavorable changes.

[0007] Most for a preservation suggested and/or, intended preservatives work bakteriostatisch and fungistatisch, occasionally also bactericidal and fungicidal: they should not be odorless and flavorless and in the sockets coming to the use after possibility soluble, toxic, strike compatible and sufficiently effective. The preservatives must, in order to be effective, be solved in the too preserving raw or auxiliary material.

Since most preservatives are better fat than water-soluble, it must be counted on the fact that z. B. in an emulsion, whose aqueous phase is to be conserved, which emigrates into the aqueous phase trained preservative in the process of the storage into the fat phase and so that the preservation of the aqueous phase is posed in question. For this reason it is advisable to use a combination of preservatives to D. h., the aqueous phase with a well water-soluble preservative to conserve the fat phase against it simultaneous with a fat-soluble preservative.

[0008] Biocides agents are used for the fight against harmful bacteria, funguses, yeast or algae in many ranges. Admitted active substances, which are frequently used in biocides compositions, e.g. are, 5-Chlor-2-Methylisothiazolin-3-on, 2-Methylisothiazolin-3-on, 2n-Octyl-isothiazolin-3-on, 4,5-Dichlor-2-n-octylisothiazolin-3-on, 1,2-Benzisothiazolin3-on and N-Alkyl-1,2-Benzisothiazolin-3-on (alkyl: C1 - C12), prefers N-Butyl-1,2Benzisothiazolin-3-on. Despite recognized good mikrobioider effectiveness this Wirkstoffklasse of the 3-Isothiazolinone is afflicted with different disadvantages. So e.g. are, the 3-Isothiazolinone as clearly sensitizing materials admits. In the sense of the consumer protection the inset of these active substances is to be kept as low therefore as possible.

[0009] Task of the invention was therefore it to indicate micro biocides compositions which are improved thereby that its components cooperate synergistically and therefore with the simultaneous inset in smaller concentrations can be used, compared to the necessary concentrations in case of the individual components.

[0010] This solve the problem the invention by biocides active substance combinations, comprising a) an effective quantity of Tetramethylolacetylendiharnstoff and b) an effective quantity one or several biocide effective materials, selected from the group of the Isothiazolin-3-one.

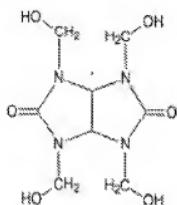
[0011] The active substance combinations according to invention show clearly synergistic effect opposite the single active substances.

[0012] Products, in particular dispersions, prefers polymer dispersions, with a content of active substance combinations according to invention are in excellent way to infestation of microorganisms and/or. Protected and for their part favorable embodiments of the present invention represent decay.

[0013] A further favorable embodiment of the present invention is the use from active substance combinations

a) an effective quantity of Tetramethylolacetylendiharnstoff and
b) an effective quantity one or several biocide effective materials, selected from the group of the Isothiazolin-3-one to the protection of products, in particular dispersions, from infestation of microorganisms and/or. Decay.

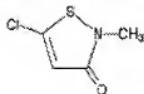
[0014] Tetramethylolacetylendiharnstoff (actually: Tetrahydro-1,3,4,6-tetrakis (hydroxymethyl) - imidazo (4,5-d) imidazol-2,5 (1H, 3H) - dion, CAS NR.: 5395-50-6) is by the chemical structure



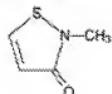
characterized.

[0015] That or the Isothiazolin-3-one from the group is preferential

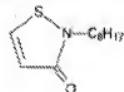
5-Chlor-2-Methylisothiazolin-3-on



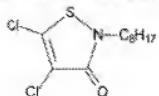
2-Methylisothiazolin-3-on.



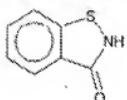
2-n-Octyl-isothiazolin-3-on,



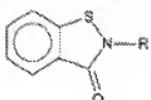
4,5-Dichlor-2-n-alkylisothiazolin-3-on



1,2-Benzisothiazolin-3-on



N-Alkyl-1,2-Benzisothiazolin-3-on



to select.

[0016] Into favorable according to invention N-Alkyl-1,2-Benzisothiazolin-3-onen R = c1 means - C12-Alkyl. The N-Butyl-1,2-Benzisothiazolin-3-on is preferential by these,

[0017] Favorably the weight ratios of A can) to b) from the range from 1000: 1 to 1: 10 to be selected, prefers 100: 1 to 1: 1, especially prefers 50: 1 to 5: 1.

[0018] Favorably the concentration of the active substance combinations according to invention can in before infestation and/or. Decay to protecting products, in particular dispersions, from the range from 0.0001 to 5.0 Gew. - %, prefers 0.01 to 1.0 Gew. -, especially prefers % 0.05 - 0.5 Gew. - % to be selected, related to the total weight of the product which can be protected.

[0019] It is appropriate, although not compelling to use the biocides of the composition according to invention in combination with a polar or nonpolar liquid medium. This medium can be given in the too preserving material for example in the biocide composition and/or.

[0020] Preferential ones polar liquid mediums are water, a aliphatischer alcohol with 1 to 4 carbon atoms, e.g. Ethanol and isopropanol, a glycol, e.g. Ethyl glycol, Diethylenglykol, 1,2-Propylenglykol, Dipropylenglykol and tri propylene glycol, a Glykoether, e.g. Butylglykol and Butyldiglykol, a glycol ester, e.g. Butyldiglykolacetat or 2,2,4-Trimethylpentandiol-monoisobutyrate, a polyethylene glycol, a polypropylene glycol, N, N-dimethyl formamide or a mixture from such materials. The polar liquid medium is in particular water.

[0021] The active substances can be present in solved form and/or in feindisperser form in the biocide compositions according to invention.

[0022] As nonpolar liquid mediums e.g. serve. Aromatics, preferably xylene and toluol.

[0023] Preparing, in particular dispersions, which active substance combinations according to invention contain, are likewise favourable embodiments of the present invention.

[0024] They can additionally still contain or several, further biocides of active substances, which are selected as a function of the area of application. Particular examples of such additional biocides active substances are in the following indicated:

[0025] Benzyl alcohol, 2,4-Dichlorbenzylalkohol, 2-Phenoxyethanol, Phenoxypropanole, phenylethyl alcohol, 5-Brom-5-nitro-1,3-dioxan, formaldehyde and formaldehyde depot materials, Dimethyldimethylhydantoin, Glyoxal, Glutardialdehyd, Sorbinsäure, benzoic acid, salicylic acid, p-Hydroxybenzoësäureester, Chloracetamid, phenols, like p-chlorinem-cresol and o-Phenylphenol, N-Methylolharnstoff, N, N' Dimethylharnstoff, Benzylalkoholhemiformal, 4,4-Dimethyl-1,3-oxazolidin, 3,3 ' - until until (5methylloxazolidine), 1,3,5-Hexahydrotriazinderivate, quaternary ammonium compounds, like e.g. N-alkyl-n, N-dimethylbenzylammoniumchlorid and the-decyldimethylammoniumchlorid, Cetylpyridiniumchlorid, Diguanidin, Polybiguanid, 1,2Dibrom-2,4-dicyanobutan, Ethylenglykolhemiformal, Tetra (hydroxymethyl) - phosphoniumsalze, 2,2-Dibrom-3-nitrilopropionsäureamid, 3-iod-2-propinyl-Nbutylcarbamat, N-Cyclohexyl-2-amino-benzthiophen-S, S-dioxide, n-aryl-N', N', dialkylharnstoffderivate like e.g. Diuron or Isoproturon, Carbendazim, Benomyl, thiabendazole, 4,5-Trimethylen-2-methylisothiazolin-3-on, 2,2 ' - Dithio dibenzoësäure those N methylamid, Triazinderivate free from chlorine from the row - Methylmercapto dialkylamino sym triazine like e.g. Terbutryn or Irgarol 1051, 2-Thiocyanomethylthiobenzthiazol, 2-Hydroxymethyl-2-nitro-1,3-propandiol, 2-Brom-2-nitropropan-1,3-diol, N, N-Until (3-aminopropyl) dodecylamin, N, N-Until (3aminopropyl) - octylamin Methylenbisthiocyanat, zinc Pyridinthion.

[0026] As such further biocides active substances are preferential 3-iod-2-propinyl-N-butylcarbamat, formaldehyde or a formaldehyde depot material as well as 2-Brom-2-nitropropan-1,3-diol.

[0027] Examples of the formaldehyde depot material are

[0028] N-formal one, like e.g. N, N' Dimethylolharnstoff, N-Methylolharnstoff, Dimethyldimethylhydantoin.

[0029] O-formal, like e.g. Ethylenglykolhemiformal, Propylenglykolhemiformal, Butyldiglykolhemiformal, Benzylalkoholhemiformal.

[0030] The biocide composition according to invention can contain beside it still different usual components, which admits to the person skilled in the art on the field of the biocides as additives are: There is e.g. this. Thickening agent, defoamer, materials for adjustment the pH value, odoriferous substances, dispersion aid and coloring materials.

[0031] The biocide composition according to invention can be used on very different fields. It is suitable for example for the inset in paints, flashes, Ligninsulfonaten, chalk mixing into a paste with, adhesives, photo chemicals, caseinhaltigen products, stärkehaltigen products, bitumen emulsions, Tensidlösungen, fuels, cleaning agents, cosmetic products, water circulations, polymer dispersions and Kühlschmierstoffen against the infestation through for example bacteria, filament eye of funguses, yeast and algae.

[0032] With the practical use the biocide composition can be brought either as finished mixture or by separate addition of the biocides and the remaining components of the composition into the too preserving material.

[0033] The biocide compositions according to invention are based on synergistic active substance combinations of Tetramethylolacetylendiharnstoff and a representative from the group of the Isothiazolin-3-one. Generally about synergy one talks, if the effectiveness of a mixture of two or several components is larger, as the sum of the effectiveness of the individual components.

[0034] An evaluation of the synergy takes place after the method from F.C. Kull et al., Applied Microbiology, 9: 538 (1961):

$$\text{Synergy index (SI)} = \frac{Qa}{QA} + \frac{Qb}{QB},$$

how

Qa = Concentration of component A in the biocide mixture with the desired effect (e.g. no growth of the microorganisms),

QA = Concentration of component A as only biocide with the desired effect,

Qb = Concentration of component B in the biocide mixture with the desired effect, and

QB = Concentration of component B as only biocide with the desired effect.

[0035] A synergy both biocides active substances exists now, if the synergy index (SI) a value of under 1 (< 1) shows.

Example 1:

[0036] With this example the synergism of combinations from Tetramethylolacetylendiharnstoff (TD) and a mixture of 5-Chloro-2-Methylisothiazolin-

3-on with 2 Methylisothiazolin-3-on becomes - in the relationship 3:1 - (CMI/MI) pointed out in the biocide composition according to invention. For this individual biocides the active substances and combinations of these active substances were trained afterwards into a commercial wall color and the effect of these mixtures on microorganisms (Pseudomonas aeruginosa, Staphylococcus aureus, Escherichia coli) was examined. The results of this testing are listed in table 1.

Tabelle 1:

Wirkstoff	Minimale Wirkstoffkonzentration (ppm), bei der noch Wirkung gegen Mikroorganismen auftritt	Synergie Index (SI)
TD	250	~
CMI/MI	18	~
TD + CMI/MI	125 ± 5	0.78

Example 2

[0037] With this example the synergism is pointed out by combinations of Tetramethylolacetylendiharnstoff (TD) and 2-Methylisothiazolin-3-on (MI) in the biocide composition according to invention. For this individual biocides the active substances and combinations of these active substances in a commercial wall color were trained and afterwards the effect of these mixtures on microorganisms (Pseudomonas aeruginosa, Staphylococcus aureus, Escherichia coli) was examined. The results of this testing are listed in table 2.

Tabelle 2:

Wirkstoff	Minimale Wirkstoffkonzentration (ppm), bei der noch Wirkung gegen Mikroorganismen auftritt	Synergie Index (SI)
TD	250	~
MI	200	~
TD + MI	125 ± 30	0.85

Example 3:

[0038] With this example the synergism is pointed out by combinations of Tetramethylolacetylendiharnstoff (TD) and 1,2-Benzisothiazolin-3-on (BIT) in the biocide composition according to invention. For this individual biocides the active substances and combinations of these active substances in a commercial wall color were trained and afterwards the effect of these mixtures on microorganisms (Pseudomonas aeruginosa, Staphylococcus aureus, Escherichia coli) was examined. The results of this testing are listed in table 3.

< tb> < TABLE> Id=Tabelle 3: Columns=3

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< tb> Head Col 1: Active substance

< tb> Head Col 2: Minimum active substance concentration (ppm), with which still effect arises against microorganisms < tb> Head Col 3: Synergy index (SI)

Tabelle 3:

Wirkstoff	Minimale Wirkstoffkonzentration (ppm), bei der noch Wirkung gegen Mikroorganismen auftritt	Synergie Index (SI)
TD	250	--
BIT	200	--
TD + BIT	125 + 30	0,65

CLAIMS

1. Biocides active substance combinations, comprising

a) an effective quantity of Tetramethylolacetylendiharnstoff and b) an effective quantity of two or several biocide effective materials, selected from the group of 2-n-Octyl-isothiazolin-3-on, 4,5-Dichlor-2-n-octylisothiazolin-3-on, 2Methylisothiazolin-3-on, 1,2-Benzisothiazolin-3-on and the n (C1-C12) - Alkyl-1,2Benzisothiazolin-3-one.

2. Use from active substance combinations

a) an effective quantity of Tetramethylolacetylendiharnstoff and b) an effective quantity of several biocide effective materials, selected from the group of 2-n-Octyl-isothiazolin-3-on, 4,5-Dichlor-2-n-octylisothiazolin-3-on, 2-Methylisothiazolin-3-on, 1,2-Benzisothiazolin-3-on and the n (C1-C12) - Alkyl-1,2Benzisothiazolin-3-one to the protection of products, in particular dispersions, from infestation of microorganisms and/or. Decay.

3. Active substance combinations or use according to claim 3, characterized in that as n (C1-C12) - Alkyl-1,2-Benzisothiazolin-3-on the N-Butyl-1,2-Benzisothiazolin-3-on is selected.

4. Active substance combinations according to claim 1 or use according to claim 2, characterized in that the weight ratios of A) to the b) from the range of 1000: 1 to 1: 10 to be selected, prefers 100: 1 to 1: 1, especially prefers 50: 1 to 5: 1.

5. Active substance combinations according to claim 1 or use according to claim 2, characterised in that the concentration of the active substance combinations in before infestation and/or. Decay to protecting products, in particular dispersions prefers polymer dispersions, from the range from 0,0001 to 5,0 Gew. - %, prefers 0,01 to 1,0 Gew. -, especially prefers % 0,05 - 0,5 Gew. - % to be selected, related to the total weight of the product which can be protected.